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**NAIL COATING COMPOSITIONS**  
**CONTAINING MICROSPHERES**

This application is a continuation-in-part of pending U.S. Patent Application Serial No. 09/186,372, filed November 5, 1998.

The subject of this invention is a colorless or colored nail coating composition containing microspheres.

Nail coatings must have good adhesion to the nail surface and the film formed on the nail by such coatings must exhibit good flexibility and strength. Generally, the industry has used modified resins to confer adhesion and plasticizers to confer flexibility to the coating.

Another important attribute of a good nail coating is abrasion resistance. Thus, nail coatings, particularly long-wearing coatings, should have all of these characteristics: abrasion resistance, adhesion, flexibility and strength. The abrasion resistance is generally achieved by incorporating fibrous materials such as Kevlar™ (Aramide fibers) into the nail coating compositions to improve the durability of the coating. One such example is described in U.S. Patent 5,370,866, where aramide fibers are incorporated into conventional nail polish ingredients at a level of about 0.01% to 0.5%. This nail composition exhibits improved abrasion resistance characteristics and film strength. Other materials useful for achieving abrasion resistance may include sand, but sand is not uniform and has rough edges which tend to snag and catch on garments or even scratch the body.

Another desirable characteristic of a nail coating is its ability to impart texture to smooth nails or to level off rough nails by filling ridges in the nails. Attempts to improve both abrasion resistance and texture have included the use of talc in nail polish compositions. However the addition of talc negatively affects the rheology and stability of the final product due to the absorption characteristics of the talc.

Thus, there is a need for a nail coating composition which can resist abrasion while still providing the desired texture or smoothness, adhesion, flexibility, and strength.

It has been unexpectedly found by the inventors that the addition of microspheres to a nail coating composition can improve adhesion to the nail while

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providing extended wear, improved mar or scuff (i.e., abrasion) resistance, and/or improved leveling and application of the nail coating. The use of microspheres can also give an appealing texture as well as a matte characteristic. Furthermore, the inventors have discovered that the addition of microspheres has little to no detrimental effect on the gloss of the resulting nail coating. In fact the nail coating compositions containing microspheres can actually enhance gloss. Also, there is no negative effect on the rheology or on the stability of the nail coating composition.

The use of microspheres has been described for a variety of applications. German patent DE19603196 describes microspheres of average diameter  $0.5\mu$  to  $1000\mu$  as a filler in, for example, alloys, dental fillings, cosmetics, pharmaceuticals and plastics. European patent application EP 235 914 describes compositions for producing textured cellulosic or plastic surfaces which include adhesion promoters and a texture-modifying amount of microspheres. While the resulting textured surfaces have low gloss, high surface hardness, and resistance to abrasion, it is necessary to include an adhesion promoter in these compositions. U.S. Patent No. 5,212,214 describes the use of ceramic microspheres as a filler in an arylene sulfide coating composition. The resulting composition is said to improve the hardness, inertness, abrasion resistance and durability of the coating. No film formers appear to be present.

Accordingly, to achieve the advantages discussed above, among others, the present invention relates to a nail coating composition which comprises, in a cosmetically acceptable medium, microspheres and at least one film-forming substance. The present invention also relates to a nail coating composition for enhancing the gloss of a nail enamel top coat, where the composition contains microspheres of average diameter ranging from about 1 to about 12 microns, with a median diameter of less than 10 microns, and at least one film-forming substance. Also, the present invention also relates to a nail coating composition for filling ridges in or smoothing out a nail surface, where the composition contains microspheres of average diameter ranging from about 1 to about 40 microns, with a median diameter ranging from 20 to 35 microns, and at least one film-forming substance, as well as to a nail coating composition for providing texture or a matte finish to a nail surface, where the composition contains microspheres of average diameter ranging from about 50 to

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about 150 microns, with a median diameter of greater than 60 microns, and at least one film-forming substance.

In addition, the present invention is drawn to a method for enhancing the gloss of a nail coating composition by applying to a nail a base coat composition containing microspheres having an average diameter ranging from about 1 to about 12 microns, with a median diameter of less than 10 microns, and then applying a nail enamel top coat. Another object of the present invention is a method for filling ridges in or smoothing out a nail surface by applying to the nail surface a nail coating composition containing microspheres of average diameter ranging from about 1 to about 40 microns, with a median diameter ranging from 20 to 35 microns, and to a method for providing texture or a matte finish to a nail surface by applying to the nail surface a nail coating composition containing microspheres with an average diameter ranging from about 50 to about 150 microns, with a median diameter of greater than 60 microns. Finally, the present invention is drawn to a method for protecting a nail surface by applying to the nail surface a nail coating composition which comprises, in a cosmetically acceptable medium, microspheres and at least one film-forming substance.

Additional objects and advantages of the invention will be set forth in part in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objects and advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims.

Reference will now be made in detail to various embodiments of the present invention.

The presently claimed invention is drawn to a nail coating composition which comprises, in a cosmetically acceptable medium, microspheres and at least one film-forming substance. In one embodiment of the invention, the microspheres are included in the inventive nail coating composition in a concentration of about 0.05% to about 15% by weight relative to the total weight of the composition. In another embodiment of the invention, the microspheres are included in the nail coating composition in an amount ranging from about 0.1% to about 6% by weight relative to the total weight.

Microspheres useful in the present invention include these of glass, metal, ceramic and/or polymeric, and may be either hollow or solid or both.

When ceramic microspheres are used, they are preferably composed of hollow, spherically-shaped ceramic particles. The spherically-shaped ceramic particles are typically composed of from about 45 parts to about 60 parts by weight silica ( $\text{SiO}_2$ ), from about 25 parts to about 38 parts by weight alumina ( $\text{Al}_2\text{O}_3$ ) and up to about ten parts by weight ferric oxide ( $\text{Fe}_2\text{O}_3$ ). The particle sizes can range from about 1 to about 300 microns, with a distribution that can range from less than about 1 micron to about 12 microns, to about less than 100 microns to about 350 microns. The size and particle size distribution are dependent on the intended final use. For example, in nail coatings, the microspheres generally have an average diameter of from about 1 micron to about 200 microns and a particle size distribution of 90% below 150 microns. Examples of commercially available ceramic microspheres suitable for use in the inventive nail enamel composition include, but are not limited to, ZEEOSPHERES<sup>TM</sup> from 3M and Zeelan Industries, Saint Paul, MN, EXTENDOSPHERES<sup>TM</sup> from the PQ Corporation, Valley Forge, PA, and Bionic Bubbles from Sphere Services Inc., Oak Ridge, TN.

The microspheres according to the present invention can range in size and are generally categorized as small, medium and large. In one embodiment of the invention, small microspheres, i.e., those having an average diameter ranging from about 1 to about 12 microns, with a median diameter of less than 10 microns, are included in the nail coating composition of the invention, resulting in improved gloss, wear enhancement, and resistance to chipping. These "small" microspheres are available, e.g., as W210 ZEEOSPHERES<sup>TM</sup> from 3M/Zeelan Industries. In another embodiment of the present invention, a composition comprising these small microspheres can be used as a base coat that enhances gloss when combined with, for example, a colored nail enamel top coat. In yet another embodiment of the invention, medium microspheres, i.e., those having an average diameter ranging from about 1 to about 40 microns, with a median diameter of ranging from 20 to 35 microns, such as W610 ZEEOSPHERES<sup>TM</sup> from 3M/Zeelan Industries, are included in the inventive composition to fill in ridges in the nails. In a further embodiment of the present

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A secondary film-former may also be present in the nail coating composition of the invention. The purpose of the secondary film former is generally to strengthen the primary film-former and to improve the adhesion characteristics of the coating

composition. Secondary film-formers which may be used in the present invention include, for example, alkyd resins, polyvinyl acetate, polyester resins, acrylic and methacrylic polymers and copolymers, polyurethane resins, epoxy resins, tosylamide epoxy resins, and resins resulting from the condensation of formaldehyde with an arylsulphonamide such as toluene sulphonamide formaldehyde resin which results from the condensation of formaldehyde and toluene sulphonamide. Polyvinyl derivatives such as polyvinylbutyral as well as the copolymers described in French Patent Applications Nos. 80.07328, 81.03199 and 88.08172 may also be used as the secondary film-forming polymer. Vinyl silicone copolymers such as those described in U.S. Patent 5,032,460 or in international application WO93/23009 can be advantageously used in blends with other film-formers. These blends of film-forming polymers can be used as the secondary film-formers and may give additional properties of flexibility to the coating composition. Blends of polyurethane and acrylic resin, such as those described in European patent application EP 391 322, can also be used; however this blend may only yield intermediate properties and may not bring out the best qualities of the individual film-forming polymers. The secondary film-formers may be present in the nail coating composition in an amount ranging from about 0.1% to about 25% by weight of the composition and preferably from about 8% to about 15% by weight of the composition.

In addition to the film-formers, one skilled in the art may add at least one plasticizer to the nail coating composition of the invention for the purposes of softening and plasticizing the film-formers in order to provide better flexibility. Examples of useful plasticizers include tricresyl phosphate, benzyl benzoate, tributyl phosphate, butyl acetylricinoleate, glyceryl acetylricinoleate, dibutyl phthalate, butyl glycolate, dioctyl phthalate, butyl stearate, tributoxyethyl phosphate, triphenyl phosphate, triethyl citrate, tributyl acetylcitrate, 2-triethylhexyl acetylcitrate, dibutyl tartrate, dimethoxyethyl phthalate, diisobutyl phthalate, diamyl phthalate, camphor, glycerol triacetate, glycerol tribenzoate and mixtures thereof. The amount of plasticizer used in the inventive nail coating composition may range from about 0.5% to about 18% and preferably from about 5% to about 10% by weight relative to the total weight of the composition.

Examples of cosmetically acceptable mediums which may be used in the present invention include, but are not limited to, alkyl acetates such as methyl, ethyl, propyl or amyl acetates; alcohols such as ethyl, isopropyl, n-butyl alcohols; short chain alkanes such as pentane, cyclopentane, hexane, cyclohexane, heptane; chlorinated mediums such as methylene chloride, chloroform or methylchloroform; non-chlorinated mediums such as toluene or N-methyl-pyrrolidone; cellosolve and derivatives such as cellosolve butyl acetate, cellosolve acetate, butyl cellosolve, or ethyl cellosolve; cyclic ethers such as tetrahydrofuran or 1,4-dioxane. In one embodiment, the medium used is alkyl acetate with the alkyl portion bearing 1 to about 4 carbons. The medium or mixture of mediums may be present in the inventive composition in an amount of from about 30% to about 80% by weight relative to the total weight of the composition and more preferably from about 65% to about 78% by weight relative to the total weight of the composition.

In one embodiment of the invention, the nail coating compositions of the invention may be in the form of a mixture of microspheres and an aqueous dispersion of at least one film-forming substance. Useful aqueous dispersions of this type are set forth in U.S. Patent 5,538,717, which relates to aqueous nail polishes containing, as film-forming substance, dispersions of polyester-polyurethane or polyether-polyurethane particles such as those formerly known by the trade name SANCURE<sup>TM</sup> and sold by the Sannor Company, now known as AVALURE<sup>TM</sup> and sold by BF Goodrich. Examples of such dispersions include, but are not limited to, SANCURE 2060<sup>TM</sup> (polyester-polyurethane), SANCURE 815<sup>TM</sup> (polyester-polyurethane, now AVALURE 405<sup>TM</sup>), SANCURE 878<sup>TM</sup> (polyether-polyurethane), and SANCURE 861<sup>TM</sup> (polyether-polyurethane). Also useful is a polyether-polyurethane dispersion sold by the ICI Company under the tradename NEOREZ R974<sup>TM</sup>. Other film-forming substances which can be used in the present invention in the form of an aqueous dispersion include acrylic emulsions and polyurethanes. In this embodiment of the invention, comprising an aqueous dispersion of the primary film forming substance, the at least one film-forming substance is present in the composition in an amount of about 3% to about 50%.

Silicones and polyethylenes are most often used as the coatings for inorganic pigments and are preferred according to the present invention. Colorant materials in the nail composition may also include chips or powder of mica, diamonds, silver, aluminum, or bronze. Also useful are specialty materials giving rise to two-tone color effects, sometimes known as color flops, such as liquid crystal silicones or multi-lamellar metallic particulates, which generally can be mixed with pigments or dyes to obtain a broader spectrum of brilliant color and increased luminous reflectance. Such materials are described in, e.g., U.S. Patent No. 3,438,796; U.S. Patent No. 4,410,570; US Patent No. 4,434,010; U.S. Patent No. 4,838,648; U.S. Patent No. 4,930,866; US Patent No. 5,171,363; U.S. Patent No. 5,364,467; U.S. Patent No. 5,569,535; US Patent No. 5,607,904; U.S. Patent No. 5,624,486; U.S. Patent No. 5,658,976; US Patent No. 5,688,494; U.S. Patent No. 5,766,335; N. Häberle et al., "Right and Left Circular Polarizing Color Filters made from Crosslinkable Cholesteric LC-Silicones," Conference record of the 1991 International Display Research Conference (IEEE), pp. 57-59; R. Maurer et al., "Polarizing Color Filters made from Cholesteric LC-Silicones," SID 90 Digest (1990), pp. 110-113; H. J. Eberle et al., "Inverse Angle Dependence of the Reflection Colours of Cholesteric Polymeric Liquid Crystals mixed with Pigments," Liquid Crystals, 5(3), (1989), pp. 907-916; J. Pinsl et al., "Liquid Crystalline Polysiloxanes for Optical Once-Write Storage." J. Molec. Electr., Vol.3 (1987), pp. 9-13; and D. Makow, "Reflection and Transmission of Polymer Liquid-



Crystal Coatings and their Applications to Decorative Arts and Stained Glass, " Color Res. Applic. Vol. 11, No. 3, (1986), pp. 205-208, all of which are incorporated herein by reference in their entirety. In one embodiment, each coloring agent is present in the nail coating composition in an amount up to about 6% by weight relative to the total weight of the composition.

The nail enamel compositions of the invention may also contain a thixotropic agent or a sedimentation retardant to thicken the composition, allow better spreading on the nail and suspend the colorant. Conventional agents of this type are silicon dioxide containing compounds such as colloidal silicic acid and clays such as stearalkonium hectorite, stearalkonium bentonite or mixtures thereof. Other useful thixotropes include urea-modified thixotrope agents such as those described in U.S. Patent 4,314,924. One such thixotrope is available from BYK-Chemie under the trade name BYK-410. Most of the mediums used in nail enamel compositions cause these clays to swell, thus providing a gel with good thixotropic properties, i.e., rendering the composition capable of passing from a gelled state to a liquid state simply by stirring and from liquid to gel after standing. A composition containing such a gel thus exhibits relatively good dispersion stability without sedimentation or separation over a long period of time. The thixotrope is present in the nail enamel composition in an amount sufficient to produce a colloidal gel. For example, the thixotrope may be present in an amount of from about 0.05% to about 15% of the weight of the total composition. Preferably, the thixotrope is present in an amount of from about 0.5% to about 5% of the weight of the total composition.

In addition to the above mentioned components, the composition according to the invention may also include additives recognized by a person skilled in the art as being capable of incorporation into such a composition. For example, the composition may include at least one cosmetically active compound, which may be selected from vitamins, minerals, moisturizers, antioxidants, stimulants, protectors, hardening agents such as silica and formaldehyde/glyoxal, and UV absorbers. Any art recognized UV absorber can be used, both organic and inorganic. Additional ingredients may include anti-foaming or anti-bubbling agents, keratin and its derivatives, melanin, collagen, cystine, chitosan and its derivatives, ceramides, oligoelements, protein hydrolysates,

and phospholipids. Further, the inventive composition may also include a fast drying promoting agent.

A person skilled in the art can, without undue experimentation, select those optional additional compounds and/or their quantity, so that the advantageous properties of the composition according to the invention are not, or are not substantially, impaired by the inclusion of such additives.

The compositions of the present invention can be manufactured by thorough mixing together of all the ingredients in the amounts described in the present invention. A person skilled in the nail enamel art would readily know of satisfactory equipment with which to do so.

Another aspect of the claimed invention is a method for enhancing the gloss of a nail coating composition by applying to a nail surface a base coat composition containing microspheres with average diameter ranging from about 1 to about 12 microns, with a median diameter of less than 10 microns. When another nail composition (e.g., a top colored enamel coat) is applied on top of the base coat of the invention, the gloss is very high. Wear and chipping resistance are also improved.

Yet another aspect of the present invention is a method for smoothing out a nail surface or filling in ridges on a nail surface by applying to the nail surface a nail composition according to the invention, wherein the microspheres range in average diameter from about 1 to about 40 microns, with a median diameter of ranging from 20 to 35 microns. The products of such methods may be sold, for example, as "ridge-filling" compositions. In a further aspect, the present invention is drawn to a method for providing texture or a matte finish to a nail surface, by applying to the nail surface a nail coating composition comprising microspheres having an average diameter ranging from about 50 to about 150 microns, with a median diameter of greater than 60 microns, and at least one film-forming substance. Finally, the present invention is also drawn to a method of protecting a nail surface by applying to the nail surface a nail composition of the invention.

The examples set forth below are intended to be illustrative but not limiting.

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## EXAMPLES

Example 1

The following product was prepared as a colored, textured nail enamel composition

<u>Ingredients</u>	<u>% w/w</u>
Ethyl acetate	33.86
Butyl acetate	15.75
Nitrocellulose	10.59
Isopropyl alcohol	7.36
Heptane	4.96
Propyl acetate	4.95
Polyester resin <sup>a</sup>	4.58
Dibutyl phthalate	4.75
Butyl alcohol	1.41
Camphor	1.41
Stearalkonium hectorite	0.47
Vinyl silicone copolymer <sup>b</sup>	0.47
Etocrylene	0.47
Benzophenone-1	0.37
Dimethicone (350 centistokes)	0.10
Guanine	0.17
Bismuth oxychloride	0.48
Ferric ammonium ferrocyanide	0.05
D & C Red #7 calcium lake	0.10
Aluminum	1.70
W1012 Z-LIGHT SPHERES <sup>TMc</sup>	6.00
	100.00

<sup>a</sup>: UNIPLEX 670-P from Unitex Co.

<sup>b</sup>: Vinyl silicone copolymer VS-80 from Minnesota Mining and Manufacturing

<sup>c</sup>: W1012 Z-LIGHT SPHERES<sup>TM</sup> have a true density of 0.7 g/cc and the particle size distribution is from about 50 microns to about 105 microns, i.e., 10% of the particles have a particle size less than 50, 50% have a particle size less than 60, and 90% have a particle size less than 95 microns.

### Example 2

The following colorless product was prepared and was used as a matte nail ridge filler:

<u>Ingredients</u>	<u>% w/w</u>
Ethyl acetate	32.95
Butyl acetate	15.75
Nitrocellulose	10.86
Isopropyl alcohol	7.36
Propyl acetate	4.95
Polyester resin <sup>a</sup>	4.58
Dibutyl phthalate	4.75
Butyl alcohol	1.41
Camphor	1.41
Stearalkonium hectorite	0.47
Vinyl silicone copolymer <sup>b</sup>	0.47
Etocrylene	0.47
Benzophenone-1	0.37
Dimethicone 350 centistokes	0.10
Acrylic resin	5.00
Titanium dioxide	1.00
Panthenol solution <sup>c</sup>	4.00
Teflon <sup>®</sup> solution	0.10
W610 ZEEOSPHERES <sup>TMd</sup>	<u>1.00</u>
	100.00

- a: UNIPLEX 670-P from Unitex Co.
- b: Vinyl silicone copolymer VS-80 from Minnesota Mining and Manufacturing Co.
- c: Panthenol is in solution in a blend of ethyl acetate, heptane and alcohol
- d: W610 ZEEOSPHERES™ have a true density of 2.4 g/cc and the particle size distribution is from about 1 micron to about 40 microns (325 mesh), i.e., 10% of the particles have a particle size less than 1, 50% have a particle size less than 10, and 95% have a particle size less than 28 microns.

Example 3

The following colorless product was prepared and was used as a glossy base and top coat which provided abrasion resistance.

<u>Ingredients</u>	<u>% w/w</u>
Ethyl acetate	35.46
Butyl acetate	16.75
Nitrocellulose	15.25
Isopropyl alcohol	9.60
Propyl acetate	4.88
Polyester resin <sup>a</sup>	4.58
Dibutyl phthalate	2.00
Butyl alcohol	1.41
Camphor	1.41
Stearalkonium hectorite	0.15
Vinyl silicone copolymer <sup>b</sup>	0.47
Etocrylene	0.47
Benzophenone-1	0.37
Dimethicone (350 centistokes)	0.10
Acrylic resin <sup>c</sup>	5.00
Titanium dioxide	1.00
D & C Violet #2 solution	0.10
W210 ZEEOSPHERES <sup>TMd</sup>	<u>1.00</u>
	100.00

<sup>a</sup>: UNIPLEX 670-P from Unitex Co.

<sup>b</sup>: Vinyl silicone copolymer VS-80 from Minnesota Mining and Manufacturing

<sup>c</sup>: Rohm & Haas B66

<sup>d</sup>: W210 ZEEOSPHERES<sup>TM</sup> have a true density of 2.4 g/cc and the particle size distribution is from about 1 micron to about 12 microns i.e., 10% of the particles have a particle size of less than 1, 50% have a particle size of less than 3, and 95% have a particle size of less than 11 microns.

Example 4

The following water-based textured nail enamel composition was prepared using an aqueous dispersion of polyurethane as the film-forming substance and medium:

<u>Ingredients</u>	<u>% w/w</u>
Ethyl alcohol	2.730
De-ionized water	12.480
Sodium Magnesium Silicate	1.230
Diazolinyl Urea	0.272
Sodium Methyl Paraben	0.362
Polyester-Polyurethane Dispersion (35% dispersion)	73.202
Dimethicone Copolyol	0.456
Tetra Sodium Pyrophosphate	0.268
Red Pigment Dispersion	3.000
W1012 Z-LIGHT SPHERES™	<u>6.000</u>
	100.000

Example 5

The following colored, glossy nail coating composition was prepared:

Cosmetically Acceptable Medium(s)	48.80
Plasticizers	18.00
Acrylics	4.50
Nitrocellulose	12.50
Zeeospheres™ W210	0.50
UV absorbers	0.50
Bentone Gel	12.00
Pigments	<u>3.20</u>
	100.00

Example 6

The following colored, glossy nail coating composition was prepared:

Cosmetically Acceptable Medium(s)	35.80
Nitrocellulose	17.29
Plasticizers	15.50
Acrylics	3.50
Polyesters	2.16
Tosylamide Epoxy	5.50
UV Absorbers	0.50
Bentone Gel	14.00
W210 Zeeospheres™	0.50
Silicone polymer	0.50
Mica	1.00
Pigments	<u>4.75</u>
	100.00

Example 7

The following colored, glossy nail coating composition was prepared:

Cosmetically Acceptable Medium(s)	41.70
Plasticizer	8.20
Epoxy	5.00
Nitrocellulose	15.80
Tosylamide Formaldehyde	10.00
PTFE	0.10
Bentone Gel	12.00
W210 Zeeospheres™	0.20
Pigments and Micas	7.00
	100.00

Example 8

The following glossy base coat composition was prepared:

Plasticizer	7.80
Nitrocellulose	13.34
Epoxy	2.70
Acrylic	4.51
Polyester	2.69
Bentone Gel	12.00
Pantenol Sol.	4.00
UV Abs.	0.50
Protein Sol.	0.01
Zeeospheres™ W210	1.00
Cosmetically Acceptable Medium(s)	51.45
	100.00

Gloss readings of products with 3 mil (0.003 inch) film thickness (form 5C-opacity Leneta card) were taken to evaluate the brilliance enhancement of any colored nail enamel when base coats containing Zeeospheres™ W210 were used. Specifically, gloss readings of 3 mil thick base coats, 3 mil thick film of colored nail enamel by itself, 3 mil thick film of colored nail enamel on top of glossy base coat, and 3 mil thick film of colored nail enamel on top of a base coat containing W210 Zeeospheres™ were taken.